ORGANO-METALLIC INTERACTIONS IN SOILS: 1. REACTIONS BETWEEN A NUMBER OF METAL IONS AND THE ORGANIC MATTER OF A PODZOL B_h HORIZON

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The nature of organic matter (O.M.) in B_h horizons of podzol soils has been extensively investigated in this laboratory. Recently (7), the number-average molecular weight of this material in two different solvents was found to be 670. From the molecular weight and from ultimate and functional group analyses, the molecular formula was calculated to be $C_{21}H_{12}(COOH)_6 \cdot (OH)_5(CO)_2$.

This information provided fresh impetus for a systematic investigation of reactions between this type of O.M. and a number of metal ions and oxides likely to occur in podzol soils. It has also made it possible to express organo-metallic interactions in soils in terms of molar rather than the customary, weight ratios.

Among the methods available for the study of organo-metallic interactions, Martell and Calvin (4) list, for example, potentiometric titrations, absorption spectroscopy, electrical conductivity, oxidation potentials, and polarographic measurements. Several of these methods have been used in the present investigation.

The literature on the role of O.M. in podzolization has been reviewed recently (8, 9). While most workers agree that soil O.M. can form stable combinations with metal ions, much remains to be learned with regard to the chemical mechanism(s) involved in these reactions. Martin and Reeve (5) question the formation of chelates between soil O.M. and metals. On the other hand, Beckwith (1) maintains that transition metals can be chelated, the binding sites being the functional groups.

The writers hope that this paper will contribute to a better understanding of the reactions involved in this important field of soil science.

MATERIALS AND METHODS

The soil sample originated from the B_h horizon of the Armadale profile, a soil developed on sandy loam material in a podzol zone. The air-dry soil was ground in an agate mortar to pass an 80-mesh sieve.

Extraction of O.M.

O.M. was extracted with 0.5 *N* NaOH, using an extractant-soil ratio of 10:1. All extractions and subsequent treatments of extracts, while in the alkaline state, were done under nitrogen. Following extraction, the O.M. was passed twice over a column of Amberlite IR-120 exchange resin in the H-form and then concentrated under vacuum at room temperature to a dark-colored solution containing 3.8 mg. per ml. The ash content of this material was 0.85 per cent.

Potentiometric titrations

Potentiometric measurements have been used extensively to provide information about the composition of metal complexes. According to Chaberek and Martell (2) the pH effect is as much a property of the metal complex as its absorption intensity.

To 5 ml. of O.M. solution (0.029 mmole) in a 50-ml. beaker was added 13 ml. of distilled water and 2 ml. of *N* KCl. Standard base was added slowly in 0.1-ml. increments from a 5-ml. microburette. No increments of base were added unless pH readings had remained essentially stable for at least 5 minutes. Mixing of reagents was ensured by a magnetic stirrer and by bubbling nitrogen into the system. For titrations of metals, appropriate aliquots of 0.05 *N* solutions to provide 0.029 mmoles of each metal (Fe^{+++}, Al^{+++}, Ca^{++}, and Mg^{++} as chlorides, Ni^{++} and Cu^{++} as sulfates) were added to 15 ml. of distilled water, followed by 2 ml. of *N* KCl and enough distilled water to produce a final volume of 20 ml. Similarly, 0.029 mmoles of each metal was titrated in the presence of 0.029 mmole of O.M., 2 ml. of *N* KCl, and sufficient distilled water to make the volume to 20 ml. The titration assembly consisted of a radiometer titrator (operated manually) with glass and calomel electrodes.

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Spectrophotometric method

In many cases complex composition can be determined by a simple spectrophotometric technique, originally developed by Job (10). This method is based on the variation of optical densities of solutions containing different ratios of metal ion and complexing agent, while simultaneously maintaining a constant total concentration of reactants.

The formation of a complex can be represented by the equation $A + n\,B \rightleftarrows AB_n$, where A is the metal ion and B the ligand. To determine n, solutions of A and B of the same molar concentrations are mixed in varying proportions and their optical densities measured. The difference (Y) between each optical density found and the corresponding optical density that would have resulted if no reaction had occurred on mixing solutions of A and B is plotted against composition. The plot will show a maximum (or minimum) at the ratio of metal to ligand which corresponds to the formula of the metal complex

One- to 9-ml. aliquots of a 1.8×10^{-2} M O.M. solution and 9- to 1-ml. aliquots of aqueous 1.8×10^{-2} M solutions of Cu^{++}, Fe^{+++}, Al^{+++}, Ca^{++}, and Mg^{++} were pipetted into 200-ml. volumetric flasks. The volumes were made to mark with distilled water. The pH of all solutions was approximately 3.0. In some experiments the pH was adjusted to 5.0 with dilute NaOH solution. Optical densities were read at 650 mμ on a Beckman model B spectrophotometer after allowing the solutions to stand for one hour at room temperature.

Conductance measurements

The disappearance or formation of ions in solution is closely related to complex formation and can be observed by changes in the electrical conductance of a solution. Information concerning the combining ratios of metal ion and ligand can be obtained by this technique.

The apparatus consisted of a conductivity bridge (model RC 16B1, manufactured by Industrial Instruments Inc., Cedar Grove, N. J.) to which an all-glass dip-type conductivity cell with black-coated platinum electrodes was attached. Organic matter, 6.7 mg. (10^{-3} mmoles), dissolved in 115 ml. of water in a 200-ml. Berzelius beaker was titrated slowly with vigorous stirring with 0.01 N NaOH and 0.01 N $Ca(OH)_2$, respectively. No increments of base were added unless readings had remained constant for at least 5 minutes. All readings were corrected for increase in volume.

Complexing power of O.M. for metal ions

In order to determine how many moles of O.M. were required to prevent the flocculation of one mole of metal, the following experiments were carried out: to 3-ml. aliquots (0.20 mg./ml.) of aqueous solutions of Fe^{+++} and Al^{+++} in a series of ground-glass-stoppered 25-ml. cylinders, increasing volumes of O.M. solution (0.38 mg./ml.) were added. Each system was diluted to approximately 12 ml. with distilled water. Separate sets of solutions were adjusted with 0.1 N NaOH solution to pH 3, 5, and 7, respectively, made up to a volume of 15 ml. with distilled water, and shaken vigorously. After standing at room temperature for 24 hours, each system was checked for flocculation. The minimum amounts of O.M. required to prevent flocculation of the metals at the various pH levels, expressed in terms of molar ratios, were taken as a measure of complexing power.

Infrared spectra

Infrared spectra were taken on KBr pellets. One mg. of thoroughly dried material was ground manually with 200 mg. of oven-dry KBr in a glass mortar for 5 minutes. Then an additional 200 mg. of KBr was added and grinding continued for another 5 minutes. The mixture was transferred to a KBr disk press which was evacuated. The pellets were pressed at 20 tons total pressure for 15 minutes. Infrared spectra were recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer against a blank consisting of 400 mg. of KBr treated in the same manner as the samples.

RESULTS AND DISCUSSION

Potentiometric titrations

The formation of iron and aluminum hydroxides was indicated by inflections in curves c and d (fig. 1) at pH 3.2 and 4.5, respectively. No such inflections appeared in curves h and i, representing equimolar mixtures of metal ions and O.M. This might be taken as an indication of complex[2]

[2] The term complex is used in this investigation as defined by Chaberek and Martell (2). It refers to the formation of stable organo-metallic compounds in which bonding between metal ion and ligand can be either primarily electrostatic or mainly covalent, or intermediate between the two.

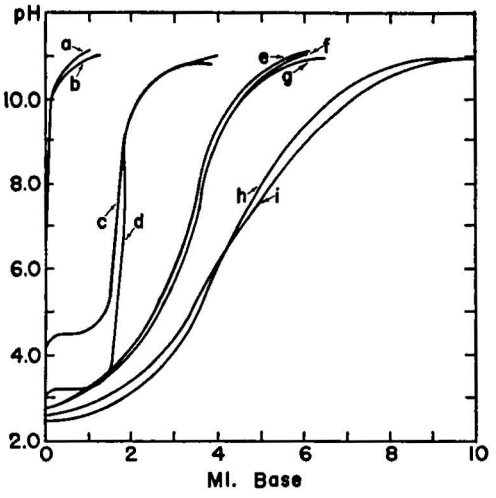

FIG. 1

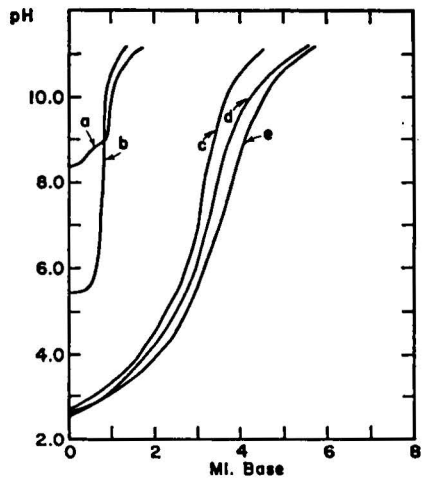

FIG. 2

FIG. 1. Titration curves for 0.029 mmoles of metal ions in the absence and presence of 0.029 mmoles (19.4 mg.) of O.M.: (*a*) Ca^{++}; (*b*) Mg^{++}; (*c*) Al^{+++}; (*d*) Fe^{+++}; (*e*) O.M.; (*f*) Ca^{++} +O.M.; (*g*) Mg^{++} +O.M.; (*h*) Fe^{+++} +O.M.; (*i*) Al^{+++} +O.M. $u = 0.1$.

FIG. 2. Titration curves for 0.029 mmoles of Ni^{++} and Cu^{++} in the absence and presence of 0.029 mmoles (19.4 mg.) of O.M.: (*a*) Ni^{++}; (*b*) Cu^{++}; (*c*) O.M.; (*d*) Ni^{++} +O.M.; (*e*) Cu^{++} +O.M. $u = 0.1$.

formation. The Ca-O.M. and Mg-O.M. curves (*f* and *g*) were for all practical purposes identical with curve *e*, produced by the titration of O.M. alone.

The formation of hydroxides was indicated by inflections in the Ni^{++} curve between approximately pH 8.4 and 9.0 (fig. 2, curve *a*) and in the Cu^{++} curve between approximately pH 5.4 and 5.6 (curve *b*). Again, in the presence of O.M. these inflections were absent (curves *d* and *e*).

The numbers of protons set free by base during the titration of 0.029 mmole of O.M. and of each of the metal ions are listed in table 1. Of special interest are the data for O.M. At pH 3, approximately one COOH group was titrated; at pH 6, five; and at pH 8, all six COOH groups had been neutralized. By pH 10 approximately two phenolic OH groups had been titrated in addition to the carboxyl groups.

The data of table 2 show that in the presence of equimolar concentrations of ferric iron and O.M., approximately 2 protons were released up to pH 8. At pH 9 and 10, the number of protons released by Fe O.M. was almost identical with that set free by Fe^{+++} alone (table 1, column 2). This is interpreted to mean that the Fe-O.M. complex started to break up at approximately pH 8 and $Fe(OH)_3$ was formed. The situation with regard to the breakup of the Al

TABLE 1

Potentiometric titrations of 0.029 mmoles of O.M., Fe^{+++}, Al^{+++}, Ni^{++}, and Cu^{++}

pH	Number of Protons Released per Mole of Base				
	O.M.	Fe^{+++}	Al^{+++}	Ni^{++}	Cu^{++}
3	1.2	—	—	—	—
4	3.2	2.7	—	—	—
5	4.4	2.9	2.4	—	—
6	5.2	2.9	2.7	—	1.3
7	5.7	3.0	2.8	—	1.5
8	6.1	3.1	2.9	—	1.6
9	6.7	3.2	3.2	1.6	1.6
10	7.6	3.7	3.7	2.0	1.7

O.M. was very similar to that of Fe O.M. Teh proton release in the presence of aluminum at low pH (3 to 6) was lower than that in presence of ferric iron. The proton release of the Ni-O.M. complex never approached that of Ni^{++} alone, attesting to considerable stability of this complex, while only at pH 10 was the number of protons set free by the Cu-O.M. interaction of the same order as that released by Cu^{++} alone.

The 2- and 3-proton release by Fe O.M. and the 1-, 2-, and 3-proton release by Al O.M. during the potentiometric titrations can be rationalized by writing the following simplified

equations, taking Fe O.M. as example (R denotes the O.M. molecule without the six carboxyl groups):

No Fe^{+++} added

(a) $$R(COOH)_6 + 6NaOH = R(COONa)_6 + 6H_2O$$
6 protons are released

Fe^{+++} added

(b) $$R(COOH)_6 + FeCl_3 + 6NaOH = R(COONa)_3 \cdot (COO)_3Fe + 3NaCl + 6H_2O$$
6 protons are released

(c) $$R(COOH)_6 + FeCl_3 + 7NaOH = R(COONa)_4 \cdot (COO)_2FeOH + 3NaCl + 6H_2O$$
7 protons are released

(d) $$R(COOH)_6 + FeCl_3 + 8NaOH = R(COONa)_5 \cdot COOFe(OH)_2 + 3NaCl + 6H_2O$$
8 protons are released

(e) $$R(COOH)_6 + FeCl_3 + 9NaOH = R(COONa)_6 + Fe(OH)_3 + 3NaCl + 6H_2O$$
9 protons are released

The data in table 2, column 2, suggest that complex formation between ferric iron and O.M. occurred according to equation (*d*), since approximately 2 protons were set free between pH 3 and 8. The predominant iron species at this pH range is in all probability $Fe(OH)_2^+$ which forms an electrovalent bond with one negatively charged carboxyl group. As the pH approaches 9, the complex breaks apart in accordance with equation (*e*), with a net release of approximately 3 protons. Complex formation according to equation (*b*) appears very unlikely, as in such case the Fe-O.M. curve would coincide with the O.M. curve. The formation of a complex involving $Fe(OH)^{++}$ (equation *c*) deserves some consideration. A net release of 1 proton is involved. The Fe O.M. released from 1.6 to 1.9 protons between pH 4 and 7. The fact that the proton release was lower than 2 might be partially due to the presence of some complexes of the type expressed by equation (*c*).

The situation with regard to aluminum appears to be similar to that of Fe^{+++}. The 1-proton release by aluminum at low pH might be due to complex formation between $Al(OH)^{++}$ and two carboxyl groups, while the 2-proton release might be ascribed to reaction between $Al(OH)_2^+$ and one negatively charged carboxyl group. Similarly the 3-proton release signalizes formation of $Al(OH)_3$ and decomposition of the organo-metallic complex. The high proton release by aluminum at pH 10 is probably due to the formation of $Al(OH)_4^-$.

The number of protons set free by the addition of Cu^{++} to O.M. (table 2, column 5) ranged from 0.8 to 1.1 between pH 3 and 8. These values are in satisfactory agreement with data reported recently by Khanna and Stevenson (3), who found proton releases per atom of Cu^{++} ranging from 0.74 to 1.04 for natural humic and fulvic acids. The value of 1.6 at pH 10 indicates the formation of the basic copper salt. The theoretical value for the neutralization of protons set free by precipitation of Cu^{++} as the basic salt is 1.66. No explanation for the proton release by Ni^{++} is offered at this time. Whether both Ni^{++} and Cu^{++} bond with one or two carboxyl groups awaits further investigation. The fact that practically no protons were released by the O.M. on addition of calcium and magnesium does not necessarily indicate the absence of complex formation. Beckwith (1) has shown that when oxalic acid was titrated with alkali, the addition of even the equivalent amount of copper did not displace the titration curve.

It is noteworthy that none of the metals precipitated during the course of the titrations, and that, on addition of all metal ions to the O.M. solution, decreases in pH, sometimes slight ones, occurred. These experiments demonstrate that one mole of O.M. could form a water-soluble complex with at least one mole of each of these metal ions. This does not exclude, as will be shown in the following paragraphs, the formation of higher complexes.

Conductance measurements

The conductometric titration of 10^{-2} mmoles of O.M. with both 0.01 N NaOH and $Ca(OH)_2$ is

illustrated (fig. 3). The shapes of these curves are essentially similar to those shown by Chaberek and Martell (2) for the conductometric titration of ethylenediaminetetraacetic acid with sodium and calcium hydroxide. An analogous interpretation has been used herein. Curve *A* is a typical conductometric neutralization curve. The minimum observed after the addition of approximately 2×10^{-2} me. of NaOH solution corresponds, in all probability, to the neutralization of two strongly acidic carboxyl hydrogens. When O.M. was titrated with $Ca(OH)_2$ (curve *B*), the first portion of the curve was similar to that of curve *A*, since no appreciable calcium complexing occurred in moderately acid solution. Further addition of $Ca(OH)_2$ solution yielded constant conductance readings, until an additional 2×10^{-2} me. of $Ca(OH)_2$ (corresponding to two more carboxyl groups), had been added. Finally, the conductance increased slightly in two steps, corresponding each time to 10^{-2} me. (or one COOH group) before rising sharply to indicate the presence of free $Ca(OH)_2$. This titration curve shows variations in the acid strength of the six carboxyl groups. The level portion of the titration curve [between 2 and 4 ml. of $Ca(OH)_2$] might be due to the disappearance of both calcium and hydroxyl ions from solution, the calcium being complexed by the O.M. and the hydroxyl reacting with hydrogen to form water. The slight stepwise rise in the titration curve [between 4 and 6 ml. of $Ca(OH)_2$] indicates, in all probability, that these two COOH groups complex calcium less strongly than the other two. The overall picture that emerges from this experiment is that out of a total of six carboxyl groups per molecular weight, two are very acidic and apparently do not react with calcium at all, two carboxyl groups complex calcium strongly, and the remaining two carboxyl groups still react with calcium but to a lesser degree. Since one mole of calcium is equal to 2

TABLE 2

Potentiometric titrations of 0.029 mmoles of O.M. in the presence of 0.029 mmoles of metal

pH	Number of Protons Released per Mole of Metal Added			
	Fe^{+++}	Al^{+++}	Ni^{++}	Cu^{++}
3	2	1.0	0.5	0.8
4	1.8	1.3	0.4	0.9
5	1.6	1.4	0.4	0.8
6	1.8	1.5	0.4	0.8
7	1.9	2.1	0.4	0.9
8	2.5	2.9	0.4	1.1
9	3.1	3.7	0.7	1.3
10	3.8	4.7	1.1	1.6

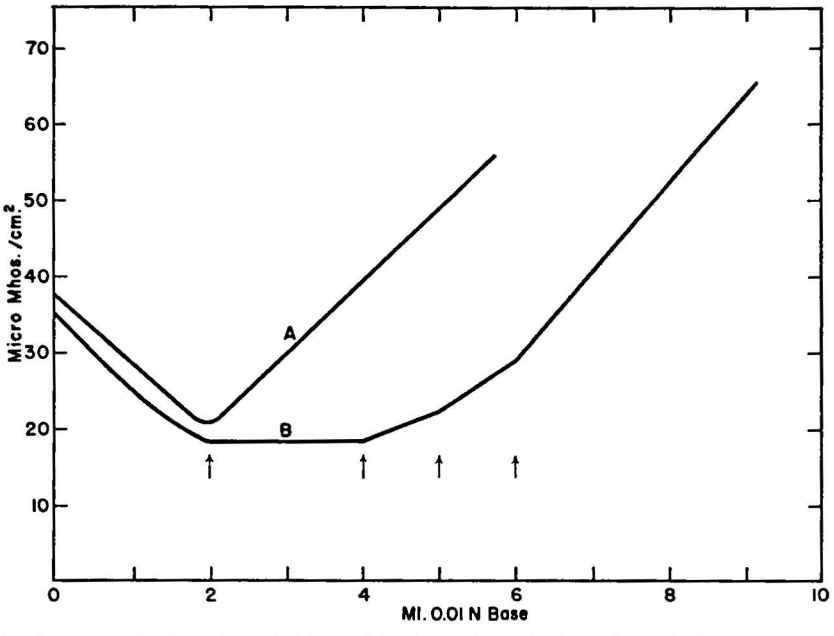

FIG. 3. Conductometric titration of O.M. with (*A*) sodium hydroxide and (*B*) calcium hydroxide

me., the molar ratio of calcium to organic matter, on the basis of this titration, is 2:1.

As has been shown in an earlier publication (7), one molecular weight of organic matter contains six carboxyl groups in addition to two phenolic and three alcoholic hydroxyls. The pH at the endpoint of the conductometric titration represented by curve *B* was 8.2, which corresponds approximately (see fig. 1, curve *e*; and table 1, column 2) to the neutralization of the six carboxyl groups. There were no indications that the phenolic hydroxyl groups participated in the reaction with calcium.

Spectrophotometric method

Absorption curves of 0.09 mmoles of O.M., 0.09 mmoles of each of O.M. and Cu^{++} and of 0.09 mmole of Cu^{++} between 450 and 800 mμ are shown in figure 4. The optical density of Cu^{++} (curve *A*) at the concentrations used in this investigation was 0.005 over the range of wavelengths examined. The optical density of the Cu-O.M. curve was higher than that of the O.M. curve, with the greatest difference between 600 and 675 mμ (curves *B* and *C*). Consequently, 650 mμ was chosen as a suitable wavelength for all further work. Figure 5 shows that the plot of optical density *vs.* concentration for the organic matter followed a straight line at 650 mμ, thus obeying Beer's law. This plot was used for the calculation of *Y* values in the Job plots at pH 5.0. A similar plot was obtained at pH 3 and used in the calculation of *Y* values at that pH. Since the optical densities of Cu^{++}, Fe^{+++} and Al^{+++} even

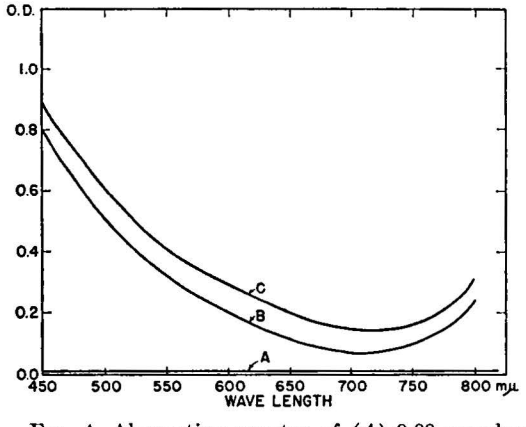

FIG. 4. Absorption spectra of (*A*) 0.09 mmoles of Cu^{++}; (*B*) 0.09 mmoles (60.3 mg) of O.M.; (*C*) 0.09 mmoles of Cu^{++} + 0.09 mmoles of O.M. Final volume, 200 ml. pH 5.

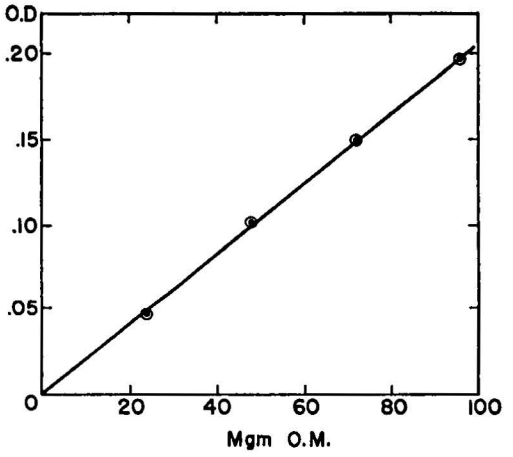

FIG. 5. Plot of optical density *vs.* concentration of O.M. at pH 5.

at the highest concentrations used in these experiments were less than 0.01, they were neglected in calculating *Y* values.

Job plots for complexes of O.M. with copper, ferric iron, and aluminum at pH 3 and 5 are shown in figure 6. At pH 3, 1:1 molar complexes were formed with copper, ferric iron, and aluminum, whereas at pH 5, copper and iron formed 2:1 molar complexes, while the Al-O.M. complex remained at 1:1.

The composition of the complexes remained essentially unaltered when optical densities were determined after allowing the solutions to stand for 24 hours, although slight flocculation occurred in some of the solutions after several hours of standing. This suggested that a slight increase in the ratio of metal to O.M. could cause the formation of insoluble complexes.

In the case of calcium and magnesium it was not possible to obtain reliable Job plots, because differences in the *Y* values at different molar ratios of O.M. and metals were too small.

Complexing power of O.M. for Fe^{+++} and Al^{+++}

Data for the complexing of O.M. for Fe^{+++} and Al^{+++} showed 0.16 moles O.M. per mole of ferric iron and 1.1 mole for aluminum. One mole of O.M. prevented the flocculation of (or complexed) 6 moles of ferric iron. One carboxyl group was thus equivalent to one atom of iron. On the other hand, one mole of O.M. prevented the flocculation of approximately one mole of aluminum only, indicating a lower complexing power for aluminum than for iron. The approxi-

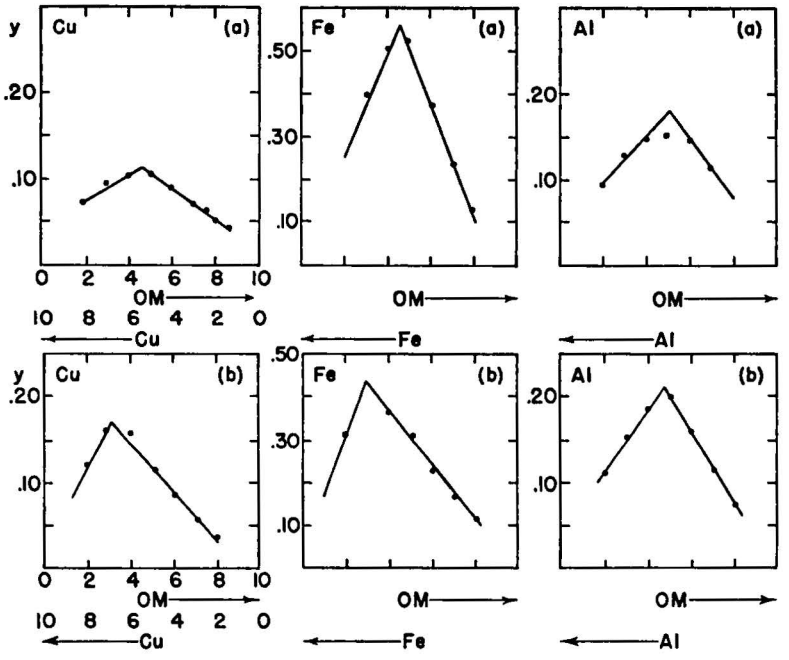

FIG. 6. Job plots for: (*a*) Cu^{++} +O.M., Fe^{+++} +O.M., Al^{+++} +O.M., all at pH 3; (*b*) Cu^{++} +O.M.; Fe^{+++} +O.M.; Al^{+++} +O.M.; all at pH 5. Figures along abscissa represent moles of each constituent.

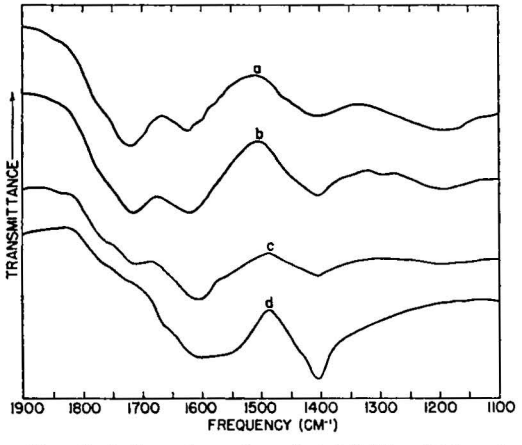

FIG. 7. Infrared spectra of: (*a*) O.M.; (*b*) 1 mole of Fe^{+++} + 1 mole of O.M.; (*c*) 3 moles of Fe^{+++} + 1 mole of O.M.; and (*d*) 6 moles of Fe^{+++} + 1 mole of O.M.

mately 1:1 molar ratio of the Al-O.M. complex is in agreement with the ratio found in the spectrophotometric studies.

In these experiments pH had no effect.

Infrared spectra

The infrared spectrum of the O.M. was identical with that shown in an earlier publication (6). The main absorption maxima were in the regions of 3400 (hydroxyl groups polymerically bonded through intermolecular hydrogen bonds), 1725 (carbonyl of carboxylic acid), 1600 (carboxylate), 1400 (carboxylate), and 1200 cm.$^{-1}$ (carboxylic acid).

On addition of increasing amounts of ferric iron, changes occurred in the 1800 to 1200 cm.$^{-1}$ regions, so only this part of the spectrum is presented herein. Figure 7 shows that in the spectrum of the O.M., the 1725 cm.$^{-1}$ band was more prominent than that at 1610 cm.$^{-1}$, while the bands at 1200 and 1400 cm.$^{-1}$ were of almost equal intensities. This indicates that possibly four out of six carboxyls were unionized, while two were ionized. As increasing amounts of iron were added (curves *b*, *c*, *d*), the intensity of the 1725 cm.$^{-1}$ band diminished while that at 1610 cm.$^{-1}$ increased. Simultaneously, the intensity of the 1400 cm.$^{-1}$ band increased while that at 1200 cm.$^{-1}$ decreased. After enough ferric iron had been added to yield a Fe-O.M. molar ratio of 6:1, both the 1725 and 1200 cm.$^{-1}$ bands completely disappeared, while those at 1610 and 1400 cm.$^{-1}$ increased in intensity. This clearly indicates that as more and more iron was added, the remaining four carboxylic acid groups also

ionized. Eventually all six carboxyl groups reacted with six atoms of iron to form iron carboxylate bonds, probably by electrovalent linkages.

To prove that the infrared spectra were interpreted correctly, the O.M. was titrated with 0.05 *N* NaOH solution to pH 7.0. The spectrum of the neutralized O.M. (not shown here) was identical with curve *d* in figure 7. This indicates that ionization of carboxyl groups is involved in the Fe-O.M. interaction. It was not possible to deduce from the spectra whether OH groups participated in the reactions with ferric iron. As more and more iron was added, the intensity of the 3400 cm.$^{-1}$ band increased rather than decreased. Assuming that OH groups were involved in the reaction with iron, one would expect a decrease in the intensity of the OH band. The fact that the intensity of the OH band increased appears to point out that iron does not react as ferric ion, but in a partially hydroxylated form, such as $Fe(OH)_2^+$ or less likely as $Fe(OH)^{++}$, and that hydroxyl groups of the partially hydroxylated ferric compounds contribute to the 3400 cm.$^{-1}$ absorption. This could mask a simultaneous decrease in absorption intensity at this frequency caused by bonding of iron with OH groups of O.M. The pH of the Fe-O.M. systems prior to the preparation of pellets was approximately 3.

When aluminum was used instead of iron, identical infrared spectra were obtained. Again, after the addition of six moles of aluminum per mole of O.M., the 1725 cm.$^{-1}$ and the 1200 cm.$^{-1}$ bands completely disappeared, while those at 1600 and 1400 cm.$^{-1}$ increased in intensity. This suggests a 6:1 molar Al-O.M. insoluble complex, involving the bonding of one carboxyl group with one atom of aluminum.

SUMMARY

Reactions between O.M., extracted from a podzol B_h horizon, and the metal ions Fe^{+++}, Al^{+++}, Ca^{++}, Mg^{++}, Cu^{++}, and Ni^{++} have been investigated by potentiometric and conductometric titrations, absorption, and infrared spectroscopy and flocculation experiments.

The O.M. formed stable water-soluble complexes with all of the metals over the pH range usually encountered in podzol soils. With the aid of the known molecular weight of the O.M., the weight ratios at which metals and O.M. combined were expressed in terms of molar ratios. While ferric iron, aluminum, and copper formed water-soluble 1:1 molar complexes with O.M. at approximately pH 3, 2:1 molar water-soluble complexes were formed at pH 5 between ferric iron, copper, calcium, and O.M. Indications were also obtained of the formation of water-insoluble 6:1 molar complexes between ferric iron, aluminum, and O.M., involving in each instance one COOH group per atom of metal. These experiments suggest the formation of a range of molar complexes, varying from 1:1 to 6:1 and becoming increasingly water-insoluble as more metal is complexed.

Evidence was procured for the formation of electrovalent bonds between negatively charged carboxyl groups of the O.M. and positively charged partially hydroxylated iron and aluminum compounds. No clear indication concerning the participation of phenolic hydroxyl groups in the organo-metallic reactions was obtained.

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